Synthesis of Composite Electrolytes with Integrated Interface Design

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Project Manager: Simon Thompson (DOE/EERE)

Project ID #BAT540

Overview

Timeline
- Start: 2021
- Finish: 2026
- 5% completed

Barriers
- Interfacial reactivity and stability
- Ion transport
- Efficiency

Budget
- Total project funding:
  - DOE Share: $2750k
- FY20: $435k
- FY21: $550k
- FY22: $550k

Partners
- Interactions/collaborations:
  - Candace Chan (ASU)
  - Chih-Long Tsai (IEK-9, FZ Jülich)
  - Dominic Bresser (HIU/KIT)
  - Andrew Westover (ORNL)

Relevance

General Objective

Develop well-controlled, scalable LLZO nanofiber and composite polymer electrolyte (CPE) synthesis processes and demonstrate the fabrication of large-area, thin CPE membranes with outstanding electro-chemo-mechanical properties.

Systems

All solid-solid battery: *solid electrodes and solid electrolytes*

Impact

The outcome of this proposal will be a transformative manufacturing solution that can create large-area, mechanically and (electro)chemically stable (0 V–4.5 V vs Li/Li^+) solid state electrolytes with Li^+ conductivity of $\geq 10^{-3}$ S/cm at room temperature enabling ≥1C charging rates.

Research Approach

- Our research philosophy is to establish a synthesis-material characterization - computation cycle that advances synthesis, chemistry, microstructure, interfaces and transport in all-solid-state lithium batteries by a coordinated, interdisciplinary approach.
- We are developing well-controlled processes for scalable LLZO nanofiber and composite polymer electrolyte (CPE) synthesis to address the manufacturing challenges of current solid-state electrolytes.
- To further improve Li^+ conductivity of CPE, we are integrating this scalable synthesis with interface design focused on Li^+ transport across the LLZO-PEO, CPE-Li and CPE-cathode interfaces.

Milestones

Month/ Year	Milestones
Sep/ 21	Characterization of chemical and electrochemical reactivity of LLZO+PEO composite with metallic Li by surface and bulk sensitive techniques. *Completed.*
Jan/ 22	Achieve uniform distribution of LLZO nanofibers within CPEs. *Completed.*
Apr/ 22	Vary LLZO doping (Al, Ga, undoped) to improve conductivity and strength. *In progress.*
Jul/ 22	Optimize LLZO nanofibers loading and processing to demonstrate good percolation and maximize conductivity. *In progress.*
Oct/ 22	Use computational methods at the continuum level for the understanding of the improved conduction pathways and lithium deposition mechanisms. *In progress.*

Motivation

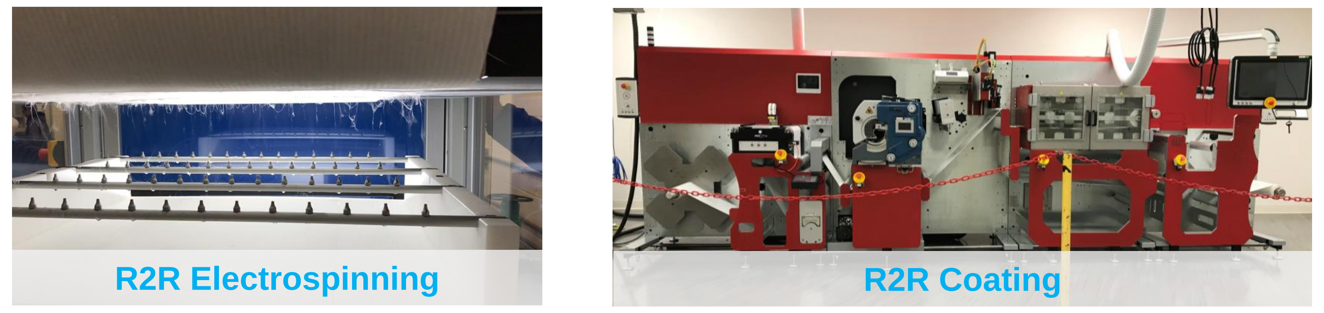
The current solid-state LLZO electrolyte is based on powder technology, which requests high processing temperatures (>1100 °C), multiple processing steps, and high production cost.

Advantages of nanofiber-based LLZO electrolytes

- Nanocrystalline grains stabilize high ionic conductivity cubic phase without dopants at low sintering temperatures (< 800 °C)
- Nanofiber non-woven structures compatible with roll-to-roll manufacturing
- Continuous 3D nanofiber network provides long-range ion transport pathways to facilitate fast charging

Nanofiber Synthesis and Composite Electrolyte Fabrication

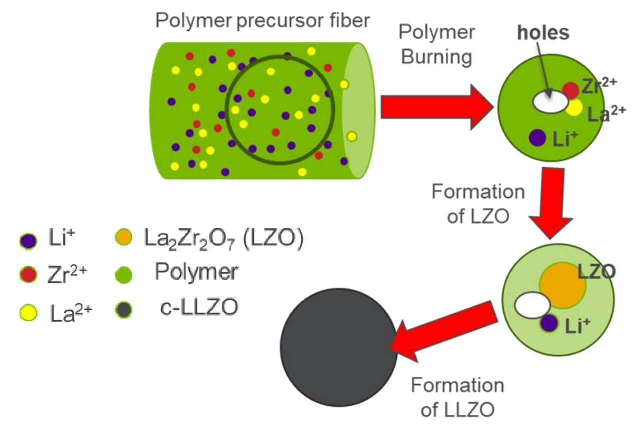
Roll-to-Roll (R2R) Manufacturing at Argonne's MERF



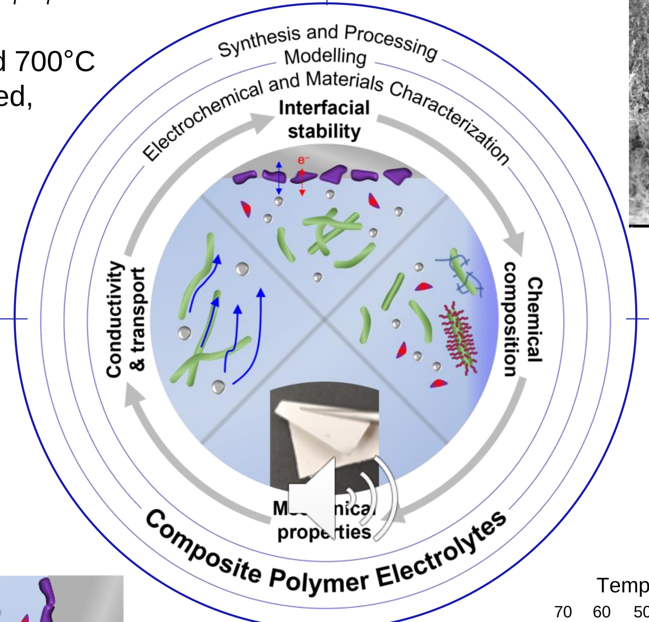
Funding support from DOE-AMO "Roll-to-Roll Advanced Materials Manufacturing DOE Laboratory Collaboration" program

- Multinozzle roll-to-roll system
- Maximum production capability: 4 m/min
- Web size: 0.5 m x 30 m
- Tunable fiber composition, geometry, and assembly configuration
- Composite materials and structures
- Roll-to-roll screen printing and slot-die coating
- Nanometer to micrometer thick membranes
- Web width 300 mm
- Corona plasma substrate preconditioning
- UV, IR and Two-zone air drying
- Built-in sensors and controls

Fiber Formation

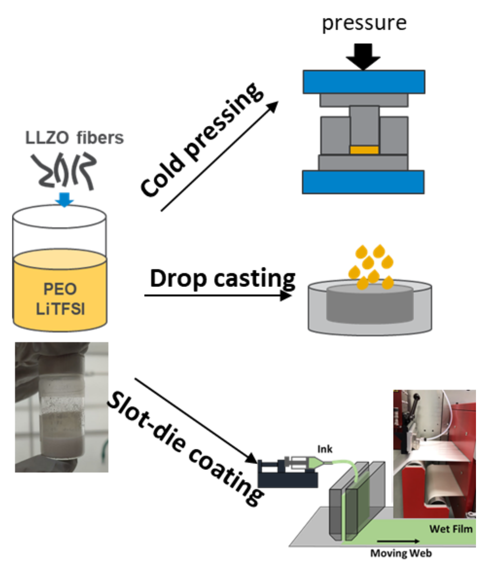


- Polymers in precursor fibers are oxidized and released at 400-500 °C, leading to the formation of $La_2Zr_2O_7$ the pores
- Clean cubic LLZO at 600°C and 700°C when all the polymers are burned, start to decompose at >800 °C

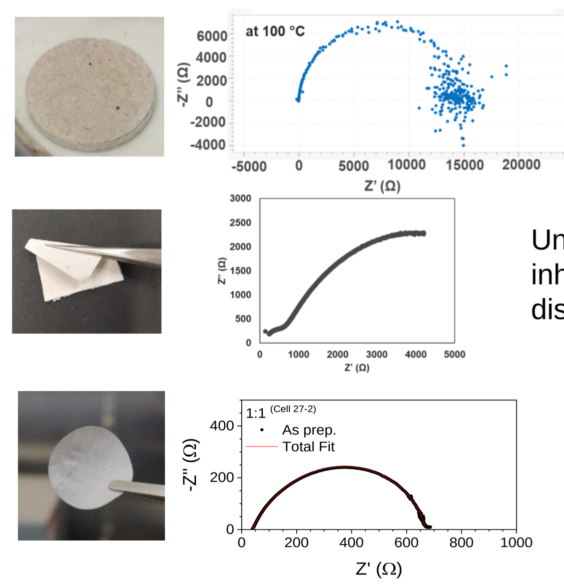


Composite Fabrication

Slurry Ink Prep



Electrolyte Film Characterization



Low density (70%), brittle, unable to cycle

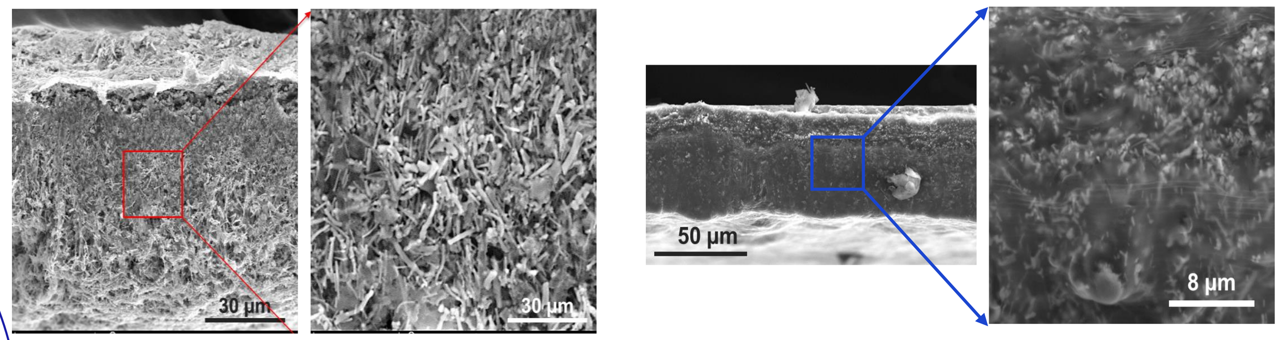
Uneven thickness, inhomogeneous fiber distribution

Precisely controlled thickness, uniform fiber distribution

Microstructure

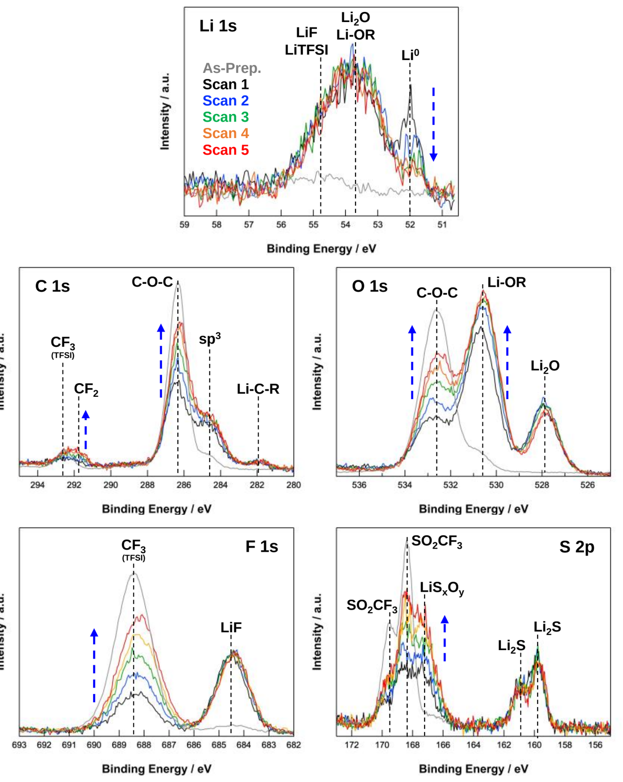
Manual Drop-Cast Sample (150 μm thickness)

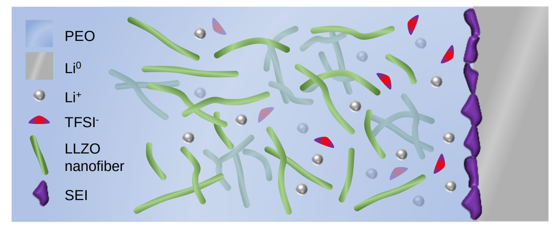
Slot-Die Coated Sample (80 μm thickness)



Interface Reactivity

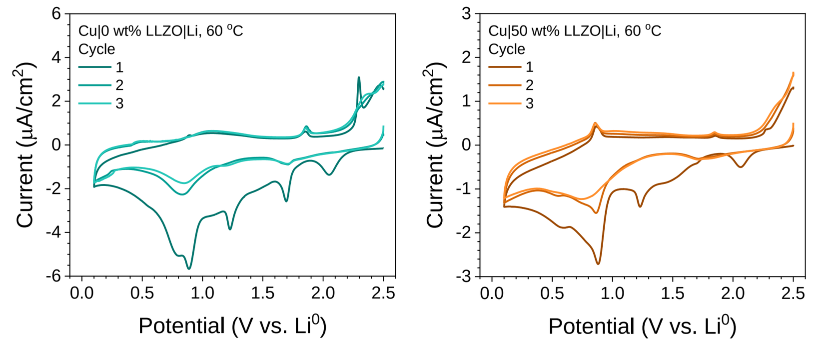
Chemical Reactivity



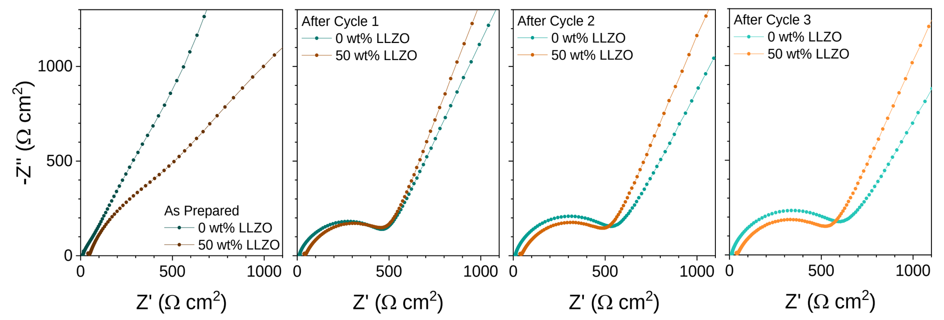


- E-beam deposited Li metal reacts with LLZO-PEO-LiTFSI composite membrane
- Lithium alkoxides and alkyllithium species form via reduction of PEO in agreement with PEO thin film reactivity with metallic Li reported previously by our group
- LiTFSI reaction with Li readily forms inorganic SEI components LiF, Li_2S, and Li_2O that are stable with time
- Li^0 peak intensity decreases and lithium alkoxide peaks continuously grow in intensity with time, indicating continuous reactivity over the timescale of the measurement
- LLZO is not in the top 5-10 nm of the interface: only PEO-LiTFSI contributes to interfacial reactivity (up to 75 wt% LLZO)

Electrochemical Reactivity

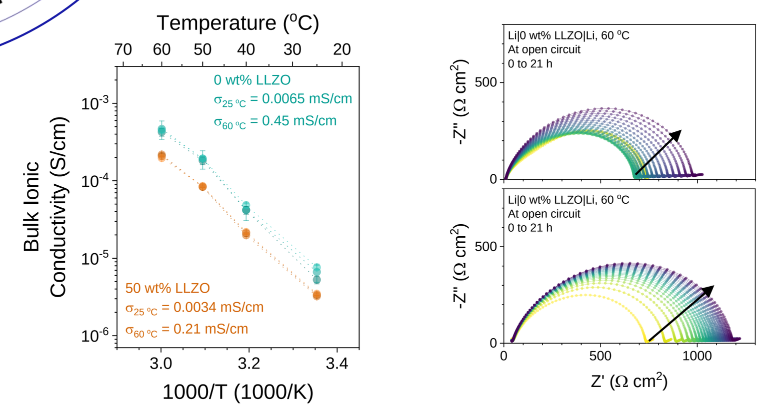


- CV redox waves and SEI impedance are nearly identical
- Electrochemical SEI formation on copper electrodes is the same with or without LLZO nanofibers

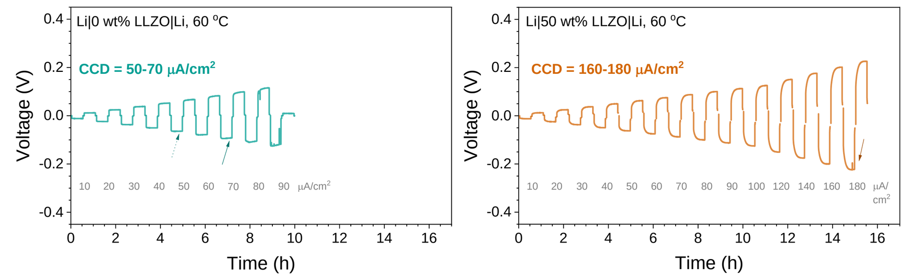


Performance

Symmetric Cell Cycling

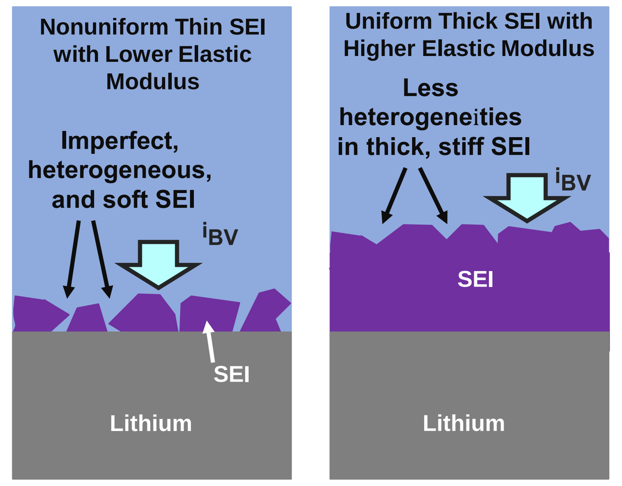


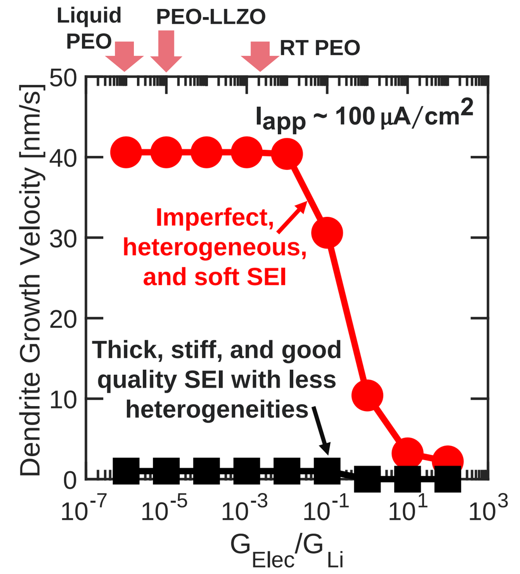
- Interface and charge transfer impedance similar with and without fibers – PEO dominates the Li-electrolyte interface
- Reduced interfacial resistance due to soft polymeric matrix
- Bulk conductivity similar between PEO and composite samples



- Good mechanical strength and integrity resulted from fiber/polymer matrix reinforced structures
- Critical current density 2-3x higher with 50 wt% LLZO nanofibers

Computation





- Thick, stiff SEI layers, with less heterogeneities tend to stabilize the lithium deposition process
- Electrolyte stiffness (G_{Elec}) can also help to suppress lithium dendrites
- Improvement in elastic modulus of the solid electrolyte due to the incorporation of the LLZO nanofibers is not significant enough to stabilize the lithium deposition process solely by mechanical means.

Remaining Barriers and Challenges

- Mechanistic understanding of differences between polymer and composite electrolyte behavior and their impact on electrochemical cycling
- Improving ionic conductivity and processability of solid electrolytes
- Control of interface properties on the cathode side to enable full cell configurations
- Control of electrochemical behavior of Li metal anode in a full cell (lithium metal and anode-free configurations) with a solid electrolyte and cathode

Proposed Future Work

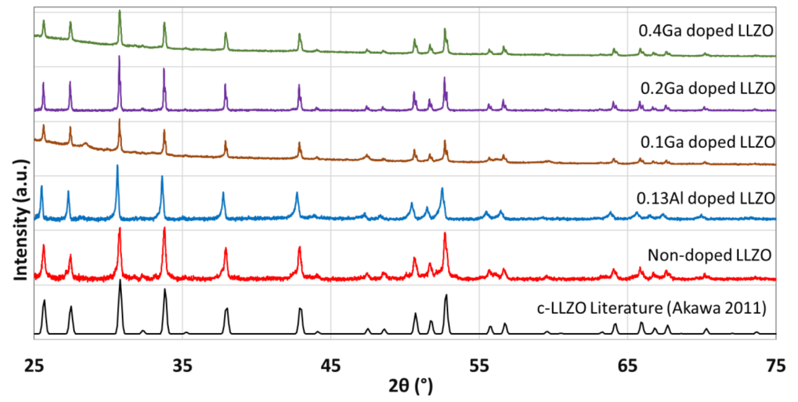
FY2022 Li-Solid Electrolyte Systems:
- Optimize microstructure and interfacial properties of composites with metallic Li
- Optimization of ionic conductivity of LLZO-PEO-LiTFSI composite electrolyte

FY2023 Toward Full cells with Li Metal Anode and Anode Free:
- Characterization of (electro)chemical reactivity of LLZO-PEO-LiTFSI composite with Li metal anode and LFP cathode by surface and bulk sensitive techniques
- Stability of interfaces in Li/SSE/cathode using experiment and theory

Any proposed future work is subject to change based on funding levels.

LLZO Dopants

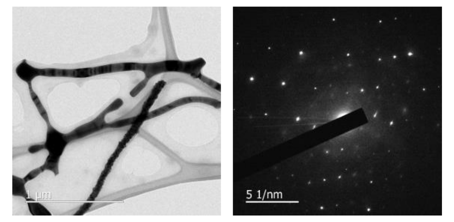
- Improve LLZO conductivity with dopant chemistry
  - Al-doped LLZO = 0.6 mS/cm
  - Ga-doped LLZO = 2.3 mS/cm
- Different dopant ratios are possible with electrospun fibers

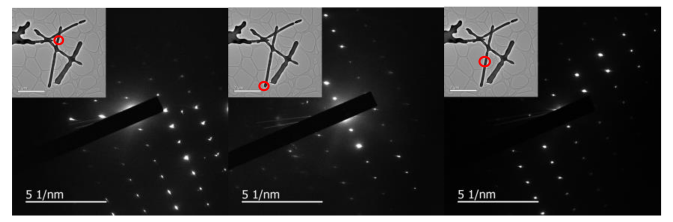


Fiber Size, Crystallinity, and Morphology

700 °C Annealed LLZO Nanofibers
- Fiber diameter ~100 nm
- Individual fibers are polycrystalline, with non-homogeneous morphology

750 °C annealed LLZO nanofibers
- Fiber diameter ~200-300 nm, length ~4 μm
- Diffraction patterns taken along fiber length direction show identical patterns: fiber is single crystalline





Response to Last Year's Comments

This is a new project.

Summary

- LLZO nanofibers can be produced efficiently in a roll-to-roll manufacturing process and incorporated into composite polymer electrolytes at high LLZO loading
- Ink composition, mechanical fluidic properties, and slot-die coating process parameters were optimized to ensure thin, dense and low-defect membranes
- Critical current density is 2-3x higher with 50 wt% LLZO nanofibers but bulk conductivity still dominated by PEO

Selected Publications and Invited Presentations

Publications:

1. **Increasing Ionic Conductivity of Poly(ethylene oxide) by Reaction with Metallic Li** P. Liu, M.J. Counihan, Y. Zhu, J.G. Connell, D. Sharon, S.N. Patel, P.C. Redfern, P. Zapol, N.M. Markovic, P.F. Nealey, L.A. Curtiss, S. Tepavcevic. *Adv. Energy Sustainability Res.*, **2022**, *3*, 2100142. (https://doi.org/10.1002/aesr.202100142)
2. **Probing Lithium Mobility at a Solid Electrolyte Surface** C. Woodahl, at al. (Submitted to *Science*)
3. **Understanding the Influence of $Li_7La_3Zr_2O_{12}$ Nanofibers on the Electrode-Electrolyte Interface in Composite Polymer Electrolytes** M.J. Counihan, D.J. Powers, P. Barai, J.G. Connell, K.S. Chavan, V. Srinivasan, Y. Zhang, S. Tepavcevic. (*In preparation*)
4. **Reduction of Nb-Doped LLZO in Contact with Li: From Surface to Bulk** M.J. Counihan, Z.D. Hood, A. Baskin, T. Li, J.G. Connell, M. Klenk, J. Zheng, D.P. Phelan, Y. Ren, D. Fong, J.W. Freeland, P. Zapol, J.W. Lawson, S. Tepavcevic. (*In preparation*)
5. **Study of phase stability of LLZO nanofibers using in-situ simultaneous SAXS and WAXS for solid-state electrolyte applications**, D. Powers, M.J. Counihan, B. Lee, M. Klenk, P. Zapol, E. Dahl, H. Seong, S. Tepavcevic, Y. Zhang. *(In preparation)*

Invited Presentations:

1. S. Tepavcevic, **Interface Reactions and Transport in Polymer and Composite Polymer Electrolytes**, MSD Colloquium, Argonne National Laboratory, January 2022.
2. S. Tepavcevic, **Advancing Solid-Solid Interfaces in Li-ion Batteries**, Solid Power, July 2021.
3. Y. Zhang, S. Tepavcevic, D. Powers, M. Koziel, M. Counihan, **$Li_7La_3Zr_2O_{12}$ Nanofiber-Based Composite Electrolyte for Solid-State Lithium Battery Applications**, Beyond Lithium-Ion XIII Conference, June 2021.
4. Y. Zhang, **Synthesis of LLZO Nanofiber for Solid-State Electrolyte Applications**, 2021 Battery Congress, May 2021.

Patents:

1. **Solid-State Nanofiber Polymer Multilayer Composite Electrolytes and Cells**, Y. Zhang, S. Tepavcevic, D. Powers, P. Zapol, J. Hryn, M. Counihan, G. Krumdick, O. Kahvecioglu, K. Pupek (Patent application filed to USPTO).